

POWDER COATING COMPOSITIONS

FIELD OF THE INVENTION

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This invention relates to powder coating compositions and to their use.

Powder coating compositions generally comprise a solid film-forming resin, usually with one or more colouring agents such as pigments, and optionally they also contain one or more performance additives. They are usually thermosetting,
10 incorporating, for example, a film-forming polymer and a corresponding curing agent (which may itself be another film-forming polymer).

The compositions are generally prepared by intimately mixing the ingredients (including any colouring agents and performance additives) for example in an extruder, at a temperature above the softening point of the film-forming polymer(s) but below a
15 temperature at which significant pre-reaction would occur. The extrudate is usually rolled into a flat sheet and comminuted, for example by grinding to the desired particle sizes ("micronising"). The size distribution required for most commercial electrostatic spray apparatus is up to 120 μ m, often between 10 and 120 μ m, with a Dv.50 within the range of 15 to 75 μ m, preferably 25 to 50 μ m, or more especially 20 to 45 μ m.

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BACKGROUND TO THE INVENTION

In the manufacture of such coating compositions speed of delivery to customers is an important consideration, but the conventional powder coatings manufacturing
25 method relies on premixing, extrusion and milling as separate processes, causing turnaround times to be long, and production of small batches of a product is not

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economic. Stocking large product ranges solves the problem of speed of delivery, but is a highly inflexible approach and is not cost-effective.

EP 372860 A describes a colour mixing process for powder coatings in which sufficiently small-sized particles ($< 20 \mu\text{m}$ in size and advantageously $< 10 \mu\text{m}$) are

5 used that mixed colours applied to a substrate have a homogeneous appearance.

Before application to the substrate the mixture is generally subjected to a process of agglomeration in which the small-sized particles are fused or bonded into composite particles, for example by mechanofusion, to convert the mixture from a cohesive mass to a free-flowing and fluidisable powder, which can be applied by conventional means.

10 Thus, a range of basic coloured powder coating compositions is produced, conventionally, in a conventional melt extrusion step, and the products are comminuted to a distinctively small particle size. A range of other colours can then be produced by mixing and agglomerating these coloured powder bases in the desired proportions.

This allows the storage of comparatively few basic coloured powder bases, which can
15 be mixed and agglomerated to produce any desired shade easily on demand, and the production of small quantities becomes commercially feasible.

EP 539385 A describes an extension of this scheme whereby the agglomeration technique is used to incorporate other film-forming or non-film-forming components to produce a range of powder coatings with a range of different
20 performance and aesthetic effects.

SUMMARY OF THE INVENTION

The present invention provides a powder coating composition in which powder
25 particles are an agglomerate of individual particulate components fused or bonded together into composite particles, wherein the individual particulate components

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comprise a first film-forming component, a coloured non-film-forming base component having a Dv.99 of no more than 30µm and comprising one or more colouring agents dispersed in a suitable carrier, and if desired one or more other components selected from film-forming and non-film-forming components.

- 5 Generally the first film-forming component is uncoloured and advantageously has a Dv.99 higher than the coloured non-film-forming base component, advantageously more than 20µm and preferably no more than 90µm.

 Accordingly, the present invention also provides a powder coating composition in which powder particles are an agglomerate of individual particulate components
10 fused or bonded together into composite particles, wherein the individual particulate components comprise

- (1) two or more coloured base components having a Dv.99 of no more than 30µm, at least one of which components is *per se* non-film-forming, and comprises one or more colouring agents dispersed in a suitable carrier, and
15 (2) one or more uncoloured film-forming components, wherein at least one component (2a) has
- (i) a Dv.99 that is more than 20µm and preferably no more than 90µm, and
(ii) a higher Dv.99 or higher Dv.50 than the coloured base components (1) taken together,
- 20 the ratio of coloured base components to uncoloured film-forming component(s) in the composition being preferably in the range of from 1:99 to 60:40, for example at least 2:98 and for example up to 30:70, by weight.

 As will be understood in the art, the volume percentiles Dv.x indicate for a stated particle size (D) the percentage (x) of the total volume of the particles that lies
25 below the stated particle size; the percentage (100-x) of the total volume lies at or above the stated size. Thus, for instance, Dv.50 is the median particle size of the

sample, and on a particle size distribution graph Dv.99 is the point on the curve read along the particle size axis where the area under the curve below this particle size represents 99% by volume of the particles. Thus, Dv.99 = 30µm indicates that 99% of the particles are below 30µm (but are not below 29µm). (For the avoidance of doubt, it should be noted that *all* particle sizes quoted herein are by volume.) Volume percentiles are measurable by laser diffraction techniques, for example by the Malvern Mastersizer.

Surprisingly, even with a high proportion of uncoloured component of significantly larger particle size than the coloured base components (whether judged according to Dv.99 or according to Dv.50), nevertheless the particles of the larger-sized component are not visible to the naked eye, so that the composition gives the appearance of a single colour.

At least one coloured base component is *per se* non-film-forming, for example being constituted as a pigment masterbatch, but having the specified particle size.

Pigment masterbatches, comprising the pigment pre-dispersed in very high concentrations in polymer material which is *per se* non-film-forming, are generally available commercially in chip or powder form. When applied to a substrate and heated, such polymers can melt and wet out on the substrate, but the masterbatches are not formulated as film-formers and contain no curing agent.

In addition, the composition may if desired contain one or more coloured base components containing film-forming polymer. Such a component may, for example, be constituted as a powder coating composition in its own right, containing the usual powder coating additives, but having the specified (reduced) particle size.

There may, for example, be one or more non-film-forming coloured base components and one or more coloured film-forming base components in the composition, each having a Dv.99 of no more than 30µm.

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An uncoloured film-forming component is usually also a powder coating composition in its own right, but having the specified particle size; there should be at least one uncoloured film-forming component having a higher Dv.99 and/or a higher Dv.50 than a coloured base component. (Usually, a component having a higher Dv.99 than another will also have a higher Dv.50 and *vice-versa*.) Usually, there are two or more coloured base components each having a Dv.99 of no more than 30 μ m and at least one uncoloured film-forming component having a Dv.99 that is more than 20 μ m and that is higher than the Dv.99 of the coloured base components taken together (or having a Dv.99 >20 μ m and a Dv.50 that is higher than the Dv.50 of the coloured base components taken together). Very often that uncoloured film-forming component will have a higher Dv.99 (or a higher Dv.50) than each coloured base component. Preferably the uncoloured film-forming component has a Dv.99 of at least 40 μ m, for example at least 50 μ m, or more than 55 μ m, e.g. in the range of from 50 to 65 μ m. Preferably it will have a Dv.90 of no more than 75 μ m and advantageously will have a Dv.50 of at least 8 μ m, especially in the range of from 12 to 30 μ m. Such uncoloured film-forming components have the advantage of lower manufacturing cost in relation to the small-sized coloured components and their use allows easy adjustment of the polymer/ pigment ratio in the composition.

The present invention also provides a kit comprising the following separate components for agglomerating into powder coating compositions for the preparation of powder coatings in a number of different colours:

- a plurality of coloured base components, each with a Dv.99 of no more than 30 μ m, at least one of which components is *per se* non-film-forming and comprises one or more colouring agents dispersed in a suitable carrier, and

- one or more uncoloured film-forming components, at least one having a Dv.99 or Dv.50 that is higher than each of the coloured base components and a Dv.99 that is more than 20µm and preferably no more than 90µm.

Such kits allow a rapid and flexible manufacture of a range of coloured powder coating compositions. The pre-dispersing of pigment in a suitable carrier, for example in a non-film-forming polymer compatible with the main film-forming component, can help maximise colour strength and provide uniformity of colour in the resulting product. The possibility of purchasing off-the-shelf products (pigment masterbatches) either of the specified size or of conventional size, for subsequent size reduction, for use in a composition of the present invention, represents a fast-track route to a colour mixing system whilst avoiding or reducing the difficult quality and cost problems associated with producing coloured powder coating base components. There is no disclosure in EP 372860 A or EP 539385 A of using a pre-dispersed pigment in a *per se* non-film-forming component (a pigment masterbatch) as one of the components in the agglomerate.

Further, in comparison with agglomerated coloured powder coating compositions described in EP 372860 A and EP 539385 A, compositions of the present invention contain a high proportion of uncoloured film-forming component, and the individual coloured components contain a significantly higher content of pigment. Moreover, the particle size of the uncoloured particles can be significantly larger than those of the coloured base components, without, surprisingly, affecting visual homogeneity. Thus, contrary to expectation and contrary to the suggestions in EP 372860 A and EP 539385 A, powders containing significant quantities of uncoloured component(s) having a Dv.99 >40µm can be used to produce powder coating films in which the differences between the coloured particles and the

uncoloured particles are not discernable by the unaided human eye. Maximising the level of larger-sized uncoloured component will give cost advantages.

The present invention also provides a powder coating composition comprising a non-agglomerated mixture of the individual particulate components specified above in
5 the specified proportions.

**DETAILED DESCRIPTION OF THE INVENTION AND DESCRIPTION OF
PREFERRED EMBODIMENTS**

- 10 The individual particulate components may comprise, for example;
- (1) two or more coloured base components each having a Dv.99 of no more than 30µm (at least one of which components is *per se* non-film-forming and comprises one or more colouring agents dispersed in a suitable carrier), in an amount of from 1 to 60% by weight of the total of components (1) and (2), and
- 15 (2)(a) one or more uncoloured film-forming components each having a Dv.99 of more than 20µm and each having a higher Dv.99 (or a higher Dv.50) than the coloured base components taken together, in an amount of from 10 to 99% by weight of the total of components (1) and (2), and, if desired,
- 20 (b) one or more other uncoloured film-forming components, in an amount of up to 30% by weight of the total of components (1) and (2).

Where there is one uncoloured film-forming component (2a) this preferably has a Dv.99 of up to 90µm, and where there are two or more uncoloured film-forming components (2a) preferably at least one, and often all, such components have a Dv.99
25 of up to 90µm.

More especially, the present invention provides a powder coating composition, suitable for providing a coating having certain appearance or performance attributes, which comprises composite particles formed by the agglomeration of individual particulate components fused or bonded together into composite particles such that the composite particles are air-fluidisable and can be applied to a substrate by electrostatic spray without causing the individual particles in the composite particles to break down under the mechanical and/or electrostatic forces associated with their application to a substrate, wherein the individual particulate components comprise

- (1) two or more coloured base components each having a Dv.99 of no more than 30µm, at least one of which components is *per se* non-film-forming and comprises one or more colouring agents dispersed in a suitable carrier, and
- (2)(a) one or more uncoloured film-forming components each having a Dv.99 of more than 20µm and preferably of no more than 90µm and each having a higher Dv.99 or Dv.50 than the coloured base components taken together,

and, if desired,

- (b) one or more other uncoloured film-forming components,

the ratio of said coloured base components to said uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 60:40, for example at least 2:98 and for example up to 30:70, by weight, and each particle of film-forming component comprising a solid polymeric binder system at least a portion of which is a film-forming resin, the resin in the composition being in an amount sufficient to impart film-forming properties to the composition.

Ratios of coloured base components (1) to uncoloured film-forming component(s) ((2a) and if desired (2b)) in the composition of from 1:99, e.g. from 2:98, preferably from 5:95, and up to 60:40, e.g. no more than 50:50, advantageously no more than 40:60 and preferably no more than 30:70, should especially be mentioned.

Advantageously, the minimum weight of uncoloured film-forming component(s) (2a) corresponds to a ratio of coloured base components (1) to uncoloured film-forming component(s) (2a) of 5:2. Preferably the weight of uncoloured film-forming component or components (2a) is at least that of coloured base components (1) and, preferably, the weight of uncoloured film-forming component(s) (2a) is at least that of other uncoloured film-forming component(s). Preferably the weight of uncoloured film-forming component(s) (2a) is at least that of components (1) and (2b) together.

The coloured base components (1) may be, for example, at least 2%, for example at least 5%, and, for example, no more than 50%, advantageously no more than 40% and preferably no more than 30%, by weight of the total of components (1) and (2). A content of coloured base component(s) of no more than 20%, for example from 10 to 20%, by weight of the total of components (1) and (2) should especially be mentioned.

The uncoloured film-forming component(s) may be, for example, at least 10%, preferably at least 20%, more preferably at least 30%, especially at least 40%, more especially at least 50%, advantageously at least 60%, for example at least 70%, and for example up to 95%, by weight of the total of components (1) and (2). A content of uncoloured film-forming component(s) of up to 90%, for example from 80 to 90%, by weight of the total of components (1) and (2) should be mentioned.

The uncoloured film-forming component(s) (2a) may be, for example, at least 10%, preferably at least 20%, more preferably at least 30%, especially at least 40%, more especially at least 50%, advantageously at least 60%, for example at least 70%, and for example up to 95%, by weight of the total of components (1) and (2).

Where the composition also includes, as particulate component in the agglomerate, a further uncoloured film-forming component (component (2b)), there may, for example, be no more than 30% by weight, calculated on all of the components (1) and (2) together, of component(s) (2b) having (i) a $D_{v.99}$ that is $\leq 20\mu\text{m}$ and (ii) a

Dv.99 (or Dv.50) that is no higher than the Dv.99 (or Dv.50 respectively) of all the coloured base components in the composition taken together. A content of uncoloured film-forming component(s) (2b) of no more than 15%, for example 10%, by weight or less, calculated on the total of components (1) and (2) should especially be mentioned.

5 If desired, the composition may include as particulate component in the agglomerate, as well as coloured base component(s) (1) and uncoloured film-forming component(s) (2a) and optionally (2b), one or more other non-film-forming components, e.g. a texturing agent, a metallic or mica pigment, or a non-film-forming performance component. If desired, such a non-film-forming component may be pre-
10 mixed with a film-forming component, e.g. with an uncoloured film-forming component, to form a masterbatch before mixing with the remaining components and then agglomerating. Alternatively, for example, a non-film-forming additive may be mixed with an uncoloured film-forming composition in an extruder and then micronised, to give an uncoloured film-forming component (2a) or (2b), depending on particle size,
15 that also contains the desired aesthetic or performance additive.

 A film-forming particulate component for inclusion in the agglomerate may itself be in the form of an agglomerate. Usually such a component would be formed by agglomeration of an uncoloured film-forming component with a non-film-forming component, for example a texturing additive or metallic or mica pigment.

20 Each film-forming component of the composition comprises at least one solid film-forming resin and includes any curing agent required therefor, and is usually formed by an extrusion process and comminution to the requisite particle size. Where a film-forming component is coloured, the colouring agent or agents (pigments and/or dyes) is (are) generally extruded with the film-forming resin(s), plus any curing agent,
25 so that particles formed therefrom comprise film-forming resin, colouring agent and, where applicable, curing agent.

Reduction of gloss, for example to satin gloss (55-65% gloss) or matt (< 30% gloss) or some other level, may be achieved by creating a surface which is rough on a microscopic scale using incompatible components or components that generate incompatibility. Film-forming components of similar chemistry but different gel times provide incompatibility during film-formation, and reduction in gloss may be achieved by such means. Usually two (or more) coloured base components are compatible with each other, but there may be an incompatible uncoloured film-forming component present. For example, film-forming components in the composition may be based on polyesters of different functionality optionally also containing a different catalyst (both of which lead to different gel times). For polyurethane systems using hydroxy-functional polyesters cured with an isocyanate (typically isopherone diisocyanate), hydroxy-functional polyesters with radically different functionality, e.g. 7 and 2, may be used. Another possibility is to employ materials that are *per se* incompatible with each other, for example a polyester and an acrylic polymer

In contrast to conventional prior art gloss-reduction processes, which generally use 50:50 non-fused mixtures of same-sized powders, with fused or bonded compositions of the present invention good gloss reduction can be achieved with substantially different proportions of gloss-reducing additive. The agglomerated material also does not suffer from particle segregation in the solid state as would dry-blended product, thus giving uniformity of product even after transportation and spraying.

In addition, or alternatively, an uncoloured film-forming component of the composition of the present invention may be compatible with the coloured base components. Usually all the coloured base components are compatible with one another.

Thus, a kit of the invention for the production of compositions with different colours and optionally different finishes may include, for example,

- two or more pigment masterbatches, or
one or more pigment masterbatches and one or more coloured film-forming base
components compatible therewith, and
 - one or more uncoloured film-forming components compatible therewith,
- 5 and optionally

- an uncoloured film-forming component incompatible therewith or that becomes
incompatible during film-formation.

Thus, an uncoloured component in the kit of the invention can be used for
extension of product ranges, giving different reduced-gloss finishes. Advantageously,
10 for any particular type of film-forming chemistry (e.g. acid-functional polyester, hydroxy-
functional polyester), a kit of the invention includes a "universal" gloss-reducing
component suitable for all powder coating compositions of that chemistry. This has the
advantage of reducing costs while also reducing stocking levels and manufacturing
capacity. It enables a very rapid and flexible service to be provided cheaply to the
15 customer, allowing for the possibility of providing small quantities of powder coating
compositions economically on request.

The present invention further provides a powder coating composition in which
powder particles are an agglomerate of individual particulate components fused or
bonded together into composite particles, wherein the individual particulate
20 components comprise

- (i) a coloured non-film-forming base component having a $Dv.99$ of no more than
30 μm and comprising one or more colouring agents dispersed in a suitable
carrier, or two or more such components, and
- (ii) an uncoloured film-forming component compatible with component(s) (i) and
25 having a $Dv.99$ that is more than 20 μm and preferably no more than 90 μm and
having a $Dv.99$ or $Dv.50$ that is higher than the $Dv.99$ or $Dv.50$ respectively of

component(s) (i), or, when there is more than one such component, of those components taken together, or two or more such components,

and, if desired,

(iii) a coloured film-forming base component compatible with components (i) and

5 (ii) and having a Dv.99 of no more than 30 μ m, or two or more such components,

and/or

(iv) an uncoloured film-forming component having a Dv.99 of more than 20 μ m and preferably no more than 90 μ m, that is incompatible with components (i) and (ii)

10 or that becomes incompatible therewith during film-formation,

and optionally one or more other components selected from film-forming and non-film-forming components.

Preferably, the pigment content of the composition is at least 0.5% by weight and the composition comprises at least 50% by weight of film-forming component(s).

15 By using different chemistries, uncoloured components can also be employed to give different performance characteristics. The different chemistries may arise, for example, from the use of different film-forming polymers, e.g. polyester and acrylic or polyester and epoxy, but may also arise from the use of different curing agents, e.g. polyester with an epoxy curing agent in one component and polyester with a bis(beta-

20 hydroxyalkylamide) curing agent such as PRIMID in another component.

An uncoloured film-forming component of a kit of the invention may be a pre-prepared uncoloured coating composition of the specified particle size or one of conventional size which is reduced in size just prior to use. A coloured non-film-forming base component of a kit of the invention may also be pre-prepared at the

25 requisite particle size, for example from a masterbatch, or may be a masterbatch of conventional particle size which is reduced in size just prior to use. Similarly, coloured

base components that are film-forming may be pre-prepared, being of the requisite particle size, or may be of larger particle size, being reduced in size just prior to use.

The number of coloured base components in a kit may be, for example, at least 7, e.g. in the range of from 7 to 30.

5 Accordingly, the present invention also provides a kit comprising the following separate components for agglomerating into powder coating compositions for the preparation of powder coatings in a number of different colours:

- at least 7 differently coloured base components, at least one of which components is non-film-forming and comprises one or more colouring agents dispersed in a
10 suitable carrier.
- an uncoloured film-forming component that is compatible with the coloured base components and remains compatible therewith during film-formation and that has a Dv.99 of more than 20 μ m and preferably of no more than 90 μ m, and
- an uncoloured film-forming component that is incompatible with the coloured base
15 components or that becomes incompatible therewith during film-formation, and that has a Dv.99 of more than 20 μ m and preferably of no more than 90 μ m.

In one embodiment of the present invention, the individual particulate components of the powder coating composition comprise

- two or more coloured base components having a Dv.99 of no more than
20 30 μ m, at least one of which components is non-film-forming and comprises one or more colouring agents dispersed in a suitable carrier, and
- one or more uncoloured film-forming components, at least one component having a higher Dv.99 or higher Dv.50 than at least one, preferably all, of the coloured base components, and preferably having a Dv.99 of more than
25 20 μ m and preferably no more than 90 μ m,

the ratio of coloured base components to uncoloured film-forming component(s) of the specified size in the composition being in the range of from 1:99 to 30:70 by weight.

In a further embodiment of the present invention, the individual particulate

5 components of the powder coating composition comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30 μ m, at least one of which components is non-film-forming, comprising one or more colouring agents dispersed in a suitable carrier, and
- one or more uncoloured film-forming components, at least one component

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having a Dv.99 of more than 40 μ m and preferably no more than 90 μ m, the ratio of coloured base components to uncoloured film-forming component(s) of the specified size in the composition being in the range of from 1:99 to 60:40 by weight.

Preferably, the uncoloured film-forming component (2a) or at least one, and

15 advantageously each, of the uncoloured film-forming components (2a) has a Dv.99 of at least 30 μ m, more especially at least 35 μ m, and advantageously at least 40 μ m. An

uncoloured film-forming component (2a) having a Dv.50 of at least 8 μ m and up to 35 μ m, e.g. up to 30 μ m, and/or having a Dv.90 of at least 14 μ m should especially be mentioned. An uncoloured film-forming component (2a) having a Dv.50 of at least

20 10 μ m and up to 35 μ m, e.g. in the range of from 12 to 30 μ m, and/or having a Dv.90 of at least 18 μ m, and one having a Dv.90 of no more than 75 μ m should also especially be mentioned.

Uncoloured component(s) (2a) may, for example, have a Dv.99 or a Dv.50 that is at least twice, e.g. at least three times, the Dv.99 or Dv.50 figure of the coloured

25 components (1) taken together. For example, the Dv.99 of component(s) (2a) may be at least 20 μ m, e.g. at least 30 μ m, more than that of components (1) taken together.

Preferably, in each of the coloured base components, whether film-forming or non-film-forming, all the component particles are $<25\mu\text{m}$. Advantageously the coloured base components have at least 90% by volume of particles $<20\mu\text{m}$, more especially at least 90% by volume $<10\mu\text{m}$, and advantageously the components have a Dv.99 of at least $6\mu\text{m}$, advantageously up to $25\mu\text{m}$. Advantageously, the Dv.50 of each such component is up to $18\mu\text{m}$, preferably up to $15\mu\text{m}$, e.g. up to $12\mu\text{m}$, advantageously at least $2\mu\text{m}$, for example within the range of for example 2 to $8\mu\text{m}$, preferably 2 to $6\mu\text{m}$ or 8 to $12\mu\text{m}$; Dv.50 sizes $\geq 2\mu\text{m}$ and $\leq 5\mu\text{m}$ should especially be mentioned.

Typically, a pigment masterbatch contains from 10 to 50% by weight of pigment, but amounts of pigment up to about 75% may also be used. Advantageously, any coloured film-forming base component contains at least 5%, especially at least 8%, by weight of pigment, calculated on the weight of that component. Advantageously, the pigment content of the coloured base components taken together is at least 5%, e.g. at least 10%, and generally no more than 70% or 75%, e.g. no more than 60%, for example 20 to 40%, by weight, calculated on the total weight of these components.

Examples of pigments which may be used in the coloured base components are inorganic pigments, such as, for example, titanium dioxide white, red and yellow iron oxides, chrome pigments and carbon black, and organic pigments such as, for example, phthalocyanine, azo, anthraquinone, thioindigo, isodibenzanthrone, triphendioxane and quinacridone pigments, vat dye pigments and lakes of acid, basic and mordant dyestuffs. Dyes may be used instead of or as well as pigments. Each coloured base component of the coating composition may contain a single colorant (pigment or dye) or may contain more than one colorant. Where appropriate, a filler may be used to assist opacity, whilst minimising costs.

Additional pigment may also be added as a separate component prior to agglomerating, especially if the pigment is close in colour to the mixed coloured base

components. Any pigment added in this way would generally be no more than 3%, preferably no more than 1%, by weight, based on the weight of the total composition, although amounts up to 5% may also be possible. Thus, for example, pigment in an amount of up to 3% by weight, more especially up to 1% by weight, may be used to
5 displace the colour of the components over a small colour region, this being used for colour tinting or colour correction of a batch.

Preferably, the total weight of pigment in the composition is at least 0.5%, more especially at least 5%, and preferably up to 30%, although an amount up to 50% is potentially also possible. The ratio of pigment to film-forming polymer component in
10 the composition may be, for example, from 1:99 to 50:50.

One or more other separate components (3) may also be present. Other optional components include, for example, performance and aesthetic additives mentioned in EP 539385 A. Those components may, if desired, be pre-mixed with another component, for example an uncoloured film-forming component, with the
15 components remaining as distinct components, e.g. (2a) and (3), before final agglomeration. Alternatively, the additives may be combined in a masterbatch with uncoloured film-forming polymer, often itself constituted as a powder coating composition in its own right, the masterbatch being prepared, for example, by co-extrusion of polymer and additive, followed by comminution, or by agglomeration of the
20 particulate additive with uncoloured film-forming powder, to form uncoloured film-forming component (2a) or (2b), often (2a). Such further aesthetics additives may be present for example in an amount of from 0.5 to 50% by weight of the total composition. A non-film-forming performance additive is generally present in an amount of no more than 5% by weight of the composition, e.g. in an amount of from 0.5
25 to 5% by weight. Where other component(s) are present in a composition of the present invention, the percentages of the specified coloured base components and/or the specified uncoloured film-forming component(s) in the composition may be altered

accordingly, but the ratio of coloured base components to uncoloured film-forming component(s) will generally remain the same.

A composition of the present invention may contain, for example, at least 1%, e.g. at least 2%, often at least 5%, by weight of the specified coloured base components. Often the composition will contain at least 20%, e.g. at least 30% or at least 40%, by weight of the uncoloured film-forming component (2a) of the size specified above. Preferably, the content of uncoloured film-forming component(s) in the composition is at least 40%, e.g. at least 50%, and advantageously at least 60%, and preferably at least 70%, by weight. Amounts of at least 40% e.g. at least 50%, and advantageously at least 60%, and preferably at least 70%, by weight of uncoloured film-forming component(s) of the size specified above should especially be mentioned.

Ratios of from 1:99, e.g. from 2:98, preferably from 5:95, and up to 60:40, e.g. up to 50:50, advantageously up to 40:60 and preferably up to 30:70, for the ratios of coloured base components (1) to uncoloured film-forming component(s) of the specified size (2a) should be mentioned.

A powder coating composition of the invention will in general be a thermosetting system, although thermoplastic systems (based, for example, on polyamides) can in principle be used instead.

When a thermosetting resin is used, the solid polymeric binder system generally includes a solid curing agent for the thermosetting resin; alternatively two co-reactive film-forming thermosetting resins may be used. Thus, a thermosetting powder coating composition according to the invention may contain one or more film-forming polymers selected from carboxy-functional polyester resins, hydroxy-functional polyester resins, epoxy resins, and functional acrylic resins. For film-forming components, carboxy-functional polyester resins should especially be mentioned.

A carboxy-functional polyester film-forming resin may be used, for example, with a polyepoxide curing agent. Such carboxy-functional polyester systems are

currently the most widely used powder coatings materials. The polyester generally has an acid value in the range 10-100, a number average molecular weight M_n of 1,500 to 10,000 and a glass transition temperature T_g of from 30°C to 85°C, preferably at least 40°C. The poly-epoxide can, for example, be a low molecular weight epoxy compound
5 such as triglycidyl isocyanurate (TGIC), a compound such as diglycidyl terephthalate condensed glycidyl ether of bisphenol A or a light-stable epoxy resin. Such a carboxy-functional polyester film-forming resin can alternatively be used with a bis(beta-hydroxyalkylamide) curing agent such as tetrakis(2-hydroxyethyl) adipamide.

Alternatively, a hydroxy-functional polyester can be used with a blocked
10 isocyanate-functional curing agent or an amine-formaldehyde condensate such as, for example, a melamine resin, a urea-formaldehyde resin, or a glycol ural formaldehyde resin, for example the material "Powderlink 1174" supplied by the Cyanamid Company, or hexahydroxymethyl melamine. A blocked isocyanate curing agent for a hydroxy-functional polyester may, for example, be internally blocked, such as the uret dione
15 type, or may be of the caprolactam-blocked type, for example isophorone diisocyanate.

As a further possibility, an epoxy resin can be used with an amine-functional curing agent such as, for example, dicyandiamide. Instead of an amine-functional curing agent for an epoxy resin, a phenolic material may be used, preferably a material formed by reaction of epichlorohydrin with an excess of bisphenol A (that is to say, a
20 polyphenol made by adducting bisphenol A and an epoxy resin). A functional acrylic resin, for example a carboxy-, hydroxy- or epoxy-functional resin can be used with an appropriate curing agent.

Mixtures of film-forming polymers can be used; for example a carboxy-functional polyester can be used with a carboxy-functional acrylic resin and a curing
25 agent such as a bis(beta-hydroxyalkylamide) which serves to cure both polymers. As further possibilities, for mixed binder systems, a carboxy-, hydroxy- or epoxy-functional

acrylic resin may be used with an epoxy resin or a polyester resin (carboxy- or hydroxy-functional). Such resin combinations may be selected so as to be co-curing, for example a carboxy-functional acrylic resin co-cured with an epoxy resin, or a carboxy-functional polyester co-cured with a glycidyl-functional acrylic resin. More usually,
5 however, such mixed binder systems are formulated so as to be cured with a single curing agent (for example, use of a blocked isocyanate to cure a hydroxy-functional acrylic resin and a hydroxy-functional polyester). Another preferred formulation involves the use of a different curing agent for each binder of a mixture of two polymeric binders (for example, an amine-cured epoxy resin used in conjunction with a
10 blocked isocyanate-cured hydroxy-functional acrylic resin).

Other film-forming polymers which may be mentioned include functional fluoropolymers, functional fluorochloropolymers and functional fluoroacrylic polymers, each of which may be hydroxy-functional or carboxy-functional, and may be used as the sole film-forming polymer or in conjunction with one or more functional acrylic,
15 polyester and/or epoxy resins, with appropriate curing agents for the functional polymers.

Other curing agents which may be mentioned include epoxy phenol novolacs and epoxy cresol novolacs; isocyanate curing agents blocked with oximes, such as isophorone diisocyanate blocked with methyl ethyl ketoxime, tetramethylene xylene
20 diisocyanate blocked with acetone oxime, and Desmodur W (dicyclohexylmethane diisocyanate curing agent) blocked with methyl ethyl ketoxime; light-stable epoxy resins such as "Santolink LSE 120" supplied by Monsanto; and alicyclic poly-epoxides such as "EHPE-3150" supplied by Daicel.

In a coloured masterbatch base component which is *per se* non-film-forming, if
25 desired the carrier may be a polymer which is capable of film-formation but with the curing agent being omitted. The use of a coloured base component which is *per se* non-film-forming, but which is cured by a curing agent present in a different component

of the composition, should be mentioned. Similarly, mention should be made of the use of a polymer, as a carrier for the pigment in the masterbatch, which is capable of film-formation but for which there is no suitable curing agent present in the composition. The use of non-functional polymers should also be mentioned.

5 The function of coatings is of course protective, but appearance is also important, and the film-forming resin and other ingredients are selected so as to provide the desired performance and appearance characteristics. In relation to performance, coatings should generally be durable and exhibit good weatherability, stain or dirt resistance, chemical or solvent resistance and/or corrosion resistance, as
10 well as good mechanical properties, e.g. hardness, flexibility or resistance to mechanical impact; the precise characteristics required will depend on the intended use. The composition must, of course, be capable of forming a coherent film on the substrate, and good flow and levelling of the composition on the substrate are required. Accordingly, the powder coating composition generally also contains one or more
15 performance additives such as, for example, a flow-promoting agent, a plasticiser, a stabiliser, for example a stabiliser against UV degradation, an anti-gassing agent, such as benzoin, or a filler. Such additives are known and standard additives for use in powder coating compositions. Usually, these performance additives will be incorporated in any film-forming component before and/or during the extrusion or other
20 homogenisation process, although, if appropriate, any such additive may alternatively be incorporated as a separate component in the agglomeration process.

Mixing and agglomeration methods are described in EP 372860 A and EP 539385 A.

25 The agglomerate may, for example, be prepared by mechanofusion of a mixture of the individual components, for example by mechanofusion at a temperature in the range of from 60 to 80°C, or by granulation using methanol or other suitable solvent as

granulating agent, to produce composite particles that constitute a free-flowing and fluidisable powder.

Good fluidity of the powder is required for purposes of application to the substrate. This fluidity of powders is governed by their particle size, and particle size
5 also controls the application efficiency of a powder; powders with small particles, i.e. significant quantities $<10\mu\text{m}$, more especially $<5\mu\text{m}$, exhibit poor fluidity and application characteristics.

The present invention also provides a process for the preparation of a powder coating composition of the present invention, which comprises providing, in the
10 specified proportions, the specified two or more coloured base components and the one or more specified uncoloured film-forming components and if desired one or more other uncoloured film-forming components and/or one or more other non-film-forming components, and mixing and agglomerating the components such that the composition is air-fluidisable and can be applied to a substrate by electrostatic spray.

15 Agglomeration prevents segregation of the constituents during application and handling, which otherwise would occur, for example during the application process itself (because of differential electrostatic charging) or in the attendant recovery and recycling process (because of differences in particle size and/or particle density) or in transport, causing batch-to-batch variability in the resulting coating.

20 The composite particles produced may be likened to raspberries with the individual particles of the raspberry (the drupels) bonded to one another, although the "drupels" are of different sizes, and there will of course also be "raspberries" of different composition and different sizes in the powder as a whole. Inspection of a fused agglomerated powder under an electron microscope shows that one particle is bonded
25 to another and that the individual particles in the composites are more rounded than prior to agglomeration. When a conventional powder coating composition is inspected

under an electron microscope, however, the powder particles are seen to be sharp-edged or angular, and are seen as separate, distinct particles - they are not fused to one another.

Further, unlike conventional uniformly coloured powder coating compositions, that contain particles of only a single colour (produced by fusion in the melt extruder), powder coating compositions of this invention consist of a mixture of differently coloured particles and uncoloured particles but nevertheless give the appearance of a single colour on application to a substrate.

An agglomerated powder coating composition according to the invention may in principle be applied to a substrate by any suitable process of powder coating technology, for example by electrostatic spray coating, or by fluidised-bed or electrostatic fluidised-bed processes.

After application of the powder coating composition to a substrate, conversion of the resulting adherent particles into a continuous coating (including, where appropriate, curing of the applied composition) may be effected by heat treatment and/or by radiant energy, notably infra-red, ultra-violet or electron beam radiation.

The powder is usually cured on the substrate by the application of heat (the process of stoving), usually for a period of from 5 to 30 minutes and usually at a temperature in the range of from 150 to 220°C, although temperatures down to 90°C may be used for some resins, especially epoxy resins; the powder particles melt and flow and a film is formed. The curing times and temperatures are interdependent in accordance with the composition formulation that is used, and the following typical ranges may be mentioned:

<u>Temperature/°C</u>	<u>Time</u>
280 to 100*	10 s to 40 min
250 to 150	15 s to 30 min
220 to 160	5 min to 20 min

- 5 • Temperature down to 90°C may be used for some resins, especially certain epoxy resins.

10 The invention also provides a process for forming a coating on a substrate, which comprises applying an agglomerated composition according to the invention to a substrate, for example by an electrostatic spray coating process, and heating the applied composition to melt and fuse the particles and where appropriate cure the coating.

15 The film may be any suitable thickness. For decorative finishes, film thicknesses as low as 20µm should be mentioned, but it is more usual for the film thickness to fall within the range 25-120µm, with common ranges being 30-80µm for some applications, and 60-120µm or, more preferably, 60-100µm for other applications, while film thicknesses of 80-150µm are less common, but not rare.

20 The substrate may comprise a metal, a heat-stable plastics material, wood, glass, or a ceramic or textile material. Advantageously, a metal substrate is chemically or mechanically cleaned prior to application of the composition, and is preferably subjected to chemical pre-treatment, for example with iron phosphate, zinc phosphate or chromate. Substrates other than metallic are in general preheated prior to application or, in the case of electrostatic spray application, are pretreated with a material that will aid such application.

25 The following Examples illustrate the invention.

EXAMPLES

Preparation of Individual Components

5 Masterbatch Components

(pigment pre-dispersed in a hydroxy-functional polyester resin, lacking curing agent)

Two pigment masterbatches were used:

10 Green Masterbatch

Phthalocyanine green pigment 50.0 g

Hydroxy-functional polyester resin 50.0 g

Red Masterbatch

15 Irgazin DPP-BO pigment 50.00 g

Hydroxy-functional polyester resin 50.00 g

The coarse particles are finely milled on a 100 AFG jet-mill from Hosakawa

Micron at a grinding air pressure of 6.0 Bar and a classifier speed of 7000 rpm.

20 The resultant particle sizes (as measured by Malvern Mastersizer X laser light-scattering device from Malvern Instruments) were as follows:

Green Masterbatch

Dv.50 = 4.7 μ m

25 Dv.90 = 10.2 μ m

Dv.99 = 12.0 μ m

Red Masterbatch

Dv.50 = 4.2 μ m

Dv.90 = 8.9 μ m

5 Dv.99 = 10.7 μ m

Film-forming components

10 A white coloured film-forming base component and an uncoloured film-forming component were prepared by mixing the following formulations.

Component A - White Powder Coating Composition

	Rutile titanium dioxide white pigment	600 g
15	Carboxylic acid-functional polyester resin	360 g
	Bis(beta-hydroxyalkylamide) curing agent	13 g
	Benzoin degassing agent	4 g
	Flow modifiers	18 g
	Surface waxes	5 g

20

Component B - Uncoloured Powder Coating Composition

	Carboxylic acid-functional polyester resin	650 g
	Bis(beta-hydroxyalkylamide) curing agent	24 g
25	Benzoin degassing agent	2 g
	Flow modifiers	18 g

Surface waxes	4 g
Fillers (barytes)	302 g

Component C - Uncoloured Powder Coating Composition for Gloss-Reduction

5

Carboxylic acid-functional polyester resin	575 g
Fillers (barytes)	333 g
Benzoin degassing agent	4 g
Surface waxes	4 g
10 Flow modifiers	18 g
Bis(beta-hydroxyalkylamide) curing agent	65 g

Component D - Uncoloured Powder Coating Composition (Polyester/Epoxy)

15	Carboxylic acid-functional polyester resin	440 g
	Glycidyl-functional Bisphenol-A epoxy resin	
	(type II or type III epoxy)	290 g
	Benzoin degassing agent	2 g
	Flow modifiers	18 g
20	Fillers (barytes)	250 g

For the coloured component A the ingredients were dry mixed and fed to an extruder blender operating at a temperature of 100°C. The extruder produced a sheet of pigmented resin which was ground to a particle size of below 100 µm and milled on
25 a 100 AFG jet-mill (manufacturer Hosakawa Micron) at 6 Bar grinding air pressure and classified at a speed of 7000 rpm. For uncoloured components B and C the procedure

was repeated except that the jet-milling was carried out at 3000 rpm. For uncoloured component D the extrudate was ground to a powder in an air-classified impact mill.

The particle size of each of the components was measured on the Malvern Mastersizer.

5 The particle size distribution for Component A was:

$$Dv.50 = 3.5\mu m$$

$$Dv.90 = 5.9\mu m$$

$$Dv.99 = 8.2\mu m$$

10 The particle size distribution (from Malvern Mastersizer X) for components B and C is:

$$Dv.50 = 18.4\mu m$$

$$Dv.90 = 36.2\mu m$$

$$Dv.99 = 51.0\mu m$$

15 The particle size distribution for component D is

$$Dv.50 = 28\mu m$$

$$Dv.90 = 58\mu m$$

$$Dv.99 = 72\mu m$$

For components A, B and D the polyester had an acid value of 18 to 30. For component C the polyester had an acid value of 40 to 90.

20

Preparation and Use of Agglomerated Powder Coating Compositions

Example 1

A mixture comprising:

25	Green Masterbatch	100.0 g
	Component A	133.0 g

Component B 767.0 g

is blended together in a Henschel FM10 mixture for a total of 30 minutes, with a heated water jacket taking the temperature to 54°C.

5 The agglomerated powder is sieved through a 110µm steel mesh and then electrostatically applied through a Gema PCG-1 spray gun onto aluminium Q panels, then stoved for 15 minutes at 200°C.

A smooth, glossy coating that has a homogeneous green colour is produced.

Example 2

10 A mixture made up from:

Red Masterbatch	120.0 g
Component A	160.0 g
Component B	720.0 g

is agglomerated, applied and cured as in Example 1.

15 A smooth, glossy coating with a homogeneous deep red colour is produced.

Example 3

A mixture made up from:

Green Masterbatch	20.0 g
20 Component A	150.0 g
Component B	700.0 g
Component C	130.0 g

is agglomerated, applied and cured as in Example 1.

A smooth, matt coating that has a pale green colour is produced.

25

Example 4

A mixture made up from:

	Green Masterbatch	80.0 g
	Red Masterbatch	40.0 g
5	Component A	40.0 g
	Component D	840.0 g

is agglomerated, applied and cured as in Example 1.

A smooth, glossy coating that has a very dark green/brown colour is produced.